

AD-A241 334



## DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

Unclassified

## 1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

## 3. DISTRIBUTION/AVAILABILITY OF REPORT

Approval for public release; distribution unlimited

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

Technical Report No. DU/DC/TR-23

## 5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION

Department of Chemistry  
Duke University6b. OFFICE SYMBOL  
(If applicable)

7a. NAME OF MONITORING ORGANIZATION

Office of Naval Research

6c. ADDRESS (City, State, and ZIP Code)

Durham, NC 27706

7b. ADDRESS (City, State, and ZIP Code)

300 North Quincy Street  
Arlington, VA 22217-50008a. NAME OF FUNDING/SPONSORING  
ORGANIZATION

Office of Naval Research

8b. OFFICE SYMBOL  
(If applicable)

## 9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

N00014-89-J-1545; R&amp;T Code 4135008

8c. ADDRESS (City, State, and ZIP Code)

800 North Quincy Street  
Arlington, VA 22217-5000

## 10. SOURCE OF FUNDING NUMBERS

PROGRAM  
ELEMENT NO.  
NRPROJECT  
NO.  
053TASK  
NO.  
841WORK UNIT  
ACCESSION NO.

## 11. TITLE (Include Security Classification)

SYNTHESIS AND CHARACTERIZATION OF COMPOUNDS CONTAINING THE  $\text{As}(\text{SiMe}_3)_2$  BRIDGING GROUP:  
CRYSTAL STRUCTURES OF  $[\text{t-Bu}_2\text{GaAs}(\text{SiMe}_3)_2]_2$ , and  $\text{t-Bu}_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{t-Bu})_2\text{Cl}$ 

## 12. PERSONAL AUTHOR(S)

L.L. Wells, A.T. McPhail, and A. Alvanipour

## 13a. TYPE OF REPORT

Technical

## 13b. TIME COVERED

FROM \_\_\_\_\_ TO \_\_\_\_\_

## 14. DATE OF REPORT (Year, Month, Day)

1991-10-03

## 15. PAGE COUNT

18

## 16. SUPPLEMENTARY NOTATION

Accepted for publication in Polyhedron.

## 17. COSATI CODES

| FIELD | GROUP | SUB-GROUP |
|-------|-------|-----------|
|       |       |           |
|       |       |           |
|       |       |           |

## 18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

gallium-arsenic, synthesis, crystal structure,  
ring compounds

## 19. ABSTRACT (Continue on reverse if necessary and identify by block number)

See attached.

91-12662



## 20. DISTRIBUTION/AVAILABILITY OF ABSTRACT

☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS

## 21. ABSTRACT SECURITY CLASSIFICATION

Unclassified

## 22a. NAME OF RESPONSIBLE INDIVIDUAL

Richard L. Wells

## 22b. TELEPHONE (Include Area Code)

(919)660-1541

## 22c. OFFICE SYMBOL

[19. ABSTRACT]

**SYNTHESIS AND CHARACTERIZATION OF COMPOUNDS  
CONTAINING THE  $\text{As}(\text{SiMe}_3)_2$  BRIDGING GROUP:  
CRYSTAL STRUCTURES OF  
 $[t\text{-Bu}_2\text{GaAs}(\text{SiMe}_3)_2]_2$  AND  
 $t\text{-Bu}_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(t\text{-Bu})_2\text{Cl}$**

Richard L. Wells\*, Andrew T. McPhail, and Abbas Alvanipour

*Department of Chemistry, Paul M. Gross Chemical Laboratory,*

*Duke University, Durham, NC 27706*

*(Received July ..., 1991)*

**Abstract**-- $[t\text{-Bu}_2\text{GaAs}(\text{SiMe}_3)_2]_2$  (I) and  $t\text{-Bu}_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(t\text{-Bu})_2\text{Cl}$  (II) were not produced from reaction mixtures of  $t\text{-Bu}_2\text{GaCl}$  with  $(\text{Me}_3\text{Si})_3\text{As}$  (1:1 and 2:1 mole ratio mixtures) and only starting materials were recovered. However,  $t\text{-Bu}_2\text{GaCl}$  reacts with  $\text{LiAs}(\text{SiMe}_3)_2 \cdot 2\text{THF}$  (1:1 mole ratio) to yield I, which on reaction with  $t\text{-Bu}_2\text{GaCl}$  (1:2 mole ratio) affords II quantitatively. Compound II is the fifth example of a compound containing the  $\text{Ga-As-Ga-X}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) core, and the second wherein the organogallium four-membered ring with arsenic, halogen mixed-bridging is not puckered. In addition to partial elemental analyses and NMR spectroscopic characterization data, the molecular structures of I and II have been elucidated by single-crystal X-ray diffraction methods. Crystal data I: monoclinic, space group  $C2/m(C^3_2h)$ ,  $a = 18.188(2) \text{ \AA}$ ,  $b = 13.017(1) \text{ \AA}$ ,  $c = 9.916(1) \text{ \AA}$ ,  $\beta = 118.54(1)^\circ$ ,  $V = 2062.4(8) \text{ \AA}^3$ ,  $Z = 2$ ; II: monoclinic, space group  $C2/c(C^6_2h)$ ,  $a = 20.872(4) \text{ \AA}$ ,  $b = 9.798(1) \text{ \AA}$ ,  $c = 19.397(4) \text{ \AA}$ ,  $\beta = 124.13(2)^\circ$ ,  $V = 3284(2) \text{ \AA}^3$ ,  $Z = 4$ .



OFFICE OF NAVAL RESEARCH

Grant NOOO14-89-J-1545

R&T Code 4135008

Technical Report No. DU/DC/TR-23

|               |                                     |
|---------------|-------------------------------------|
| Accession For |                                     |
| DTIC GRA&I    | <input checked="" type="checkbox"/> |
| DTIC TAB      | <input type="checkbox"/>            |
| Unannounced   | <input type="checkbox"/>            |
| Justification |                                     |
| Distribution  |                                     |
| Availability  |                                     |
| Avail. and/or |                                     |
| Dist          | Special                             |
| A-1           |                                     |

SYNTHESIS AND CHARACTERIZATION OF COMPOUNDS CONTAINING THE

As(SiMe<sub>3</sub>)<sub>2</sub> BRIDGING GROUP: CRYSTAL STRUCTURES OF

[*t*-Bu<sub>2</sub>GaAs(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, and *t*-Bu<sub>2</sub>GaAs(SiMe<sub>3</sub>)<sub>2</sub>Ga(*t*-Bu)<sub>2</sub>Cl

by

R. L. Wells, A. T. McPhail, and A. Alvanipour

Prepared for Publication in Polyhedron

Duke University  
Department of Chemistry  
Durham, NC 27706

October 3, 1991

Reproduction in whole or in part is permitted for  
any purpose of the United States Government

This document has been approved for public release  
and sale; its distribution is unlimited

[*Polyhedron* 1991, in press]

**SYNTHESIS AND CHARACTERIZATION OF COMPOUNDS  
CONTAINING THE As(SiMe<sub>3</sub>)<sub>2</sub> BRIDGING GROUP:  
CRYSTAL STRUCTURES OF  
[*t*-Bu<sub>2</sub>GaAs(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> AND  
 $\overline{t\text{-Bu}_2\text{GaAs(SiMe}_3)_2\text{Ga(t-Bu)}_2\text{Cl}}$**

Richard L. Wells\*, Andrew T. McPhail, and Abbas Alvanipour

*Department of Chemistry, Paul M. Gross Chemical Laboratory,  
Duke University, Durham, NC 27706*

(Received July ..., 1991)

Abstract--[*t*-Bu<sub>2</sub>GaAs(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (I) and  $\overline{t\text{-Bu}_2\text{GaAs(SiMe}_3)_2\text{Ga(t-Bu)}_2\text{Cl}}$  (II) were not produced from reaction mixtures of *t*-Bu<sub>2</sub>GaCl with (Me<sub>3</sub>Si)<sub>3</sub>As (1:1 and 2:1 mole ratio mixtures) and only starting materials were recovered. However, *t*-Bu<sub>2</sub>GaCl reacts with LiAs(SiMe<sub>3</sub>)<sub>2</sub>•2THF (1:1 mole ratio) to yield I, which on reaction with *t*-Bu<sub>2</sub>GaCl (1:2 mole ratio) affords II quantitatively. Compound II is the fifth example of a compound containing the  $\overline{\text{Ga-As-Ga-X}}$  (X = Cl, Br) core, and the second wherein the organogallium four-membered ring with arsenic, halogen mixed-bridging is not puckered. In addition to partial elemental analyses and NMR spectroscopic characterization data, the molecular structures of I and II have been

elucidated by single-crystal X-ray diffraction methods. Crystal data I: monoclinic, space group  $C2/m(C^3_2h)$ ,  $a = 18.188(2) \text{ \AA}$ ,  $b = 13.017(1) \text{ \AA}$ ,  $c = 9.916(1) \text{ \AA}$ ,  $\beta = 118.54(1)^\circ$ ,  $V = 2062.4(8) \text{ \AA}^3$ ,  $Z = 2$ ; II: monoclinic, space group  $C2/c(C^6_2h)$ ,  $a = 20.872(4) \text{ \AA}$ ,  $b = 9.798(1) \text{ \AA}$ ,  $c = 19.397(4) \text{ \AA}$ ,  $\beta = 124.13(2)^\circ$ ,  $V = 3284(2) \text{ \AA}^3$ ,  $Z = 4$ .

---

It is generally accepted that much of the impetus for the rapid growth in the number of new organogallium-arsenic compounds that have been reported since 1986 has been the quest for new gallium arsenide precursors.<sup>1</sup> As a result, considerable attention is being given to the search for new synthetic modes of forming the gallium-arsenic bond, and thus finding different pathways to new cyclic systems, clusters, and chains which may be studied further with respect to their reactivity, properties, and potential as precursors. To this end, we have been exploiting two synthetic routes, both first employed by us; namely, the metathetical elimination of (1) a silyl halide from a silylarsine and a gallium halide,<sup>2</sup> and (2) a salt from a metal arsenide and a gallium halide.<sup>3</sup> Among the compounds recently prepared and studied in our program are the cyclic mixed-bridge compounds  $R_2GaAs(SiMe_3)_2Ga(R)_2Cl$  [ $R = Me_3SiCH_2$  (III)<sup>4</sup> and  $Me_3CCH_2$  (IV)<sup>5</sup>] and the dimers  $[R_2GaAs(SiMe_3)_2]_2$  [ $R = Me_3SiCH_2$  (V)<sup>4</sup> and  $Me_3CCH_2$  (VI)<sup>5</sup>]. Moreover, in an effort to extend these studies to other III-V combinations, we very recently reported the isolation of the indium-arsenic<sup>6</sup> and indium-phosphorus<sup>7</sup> analogs of III and V,  $(Me_3SiCH_2)_2ME(SiMe_3)_2M(CH_2SiMe_3CH_2)_2Cl$  and  $[(Me_3SiCH_2)_2ME(SiMe_3)_2]_2$  ( $M = In$ ,  $E = As$  and  $P$ ).

As part of a continuing effort to expand the scope of the above gallium-arsenic series, it was deemed most appropriate for us to select *tert*-butyl as the alkyl substituent on the gallium atoms. Not only would this group add to the steric bulk around the gallium and thereby possibly influence the conformation of the ring(s) which may be formed, but any new compounds isolated should have certain desirable properties in common with the gallium arsenide *tert*-butyl containing single-source precursors recently reported by Cowley, Jones and co-workers<sup>8</sup>, and by Higa and George<sup>9</sup>. We also sought to continue to address the interesting and important matters of the reactivity and interconvertibility of these types of compounds, and herein we report our results obtained with the *tert*-butyl ligand system.

## EXPERIMENTAL

### *General information*

All manipulations and reactions were performed under vacuum, under argon in a Vacuum/Atmospheres HE-493 Dri-Lab, or under N<sub>2</sub> in standard Schlenk apparatus. Solvents were distilled from sodium/benzophenone ketyl under dry N<sub>2</sub> and degassed by several freeze-pump-thaw cycles. *t*-Bu<sub>2</sub>GaCl,<sup>9</sup> (Me<sub>3</sub>Si)<sub>3</sub>As,<sup>10</sup> and LiAs(SiMe<sub>3</sub>)<sub>2</sub>•2THF<sup>10</sup> were prepared by literature procedures. <sup>1</sup>H (300 MHz) and <sup>13</sup>C{<sup>1</sup>H} (75.4 MHz) NMR spectra were recorded on a Varian XL-300 spectrometer at ambient temperatures using C<sub>6</sub>D<sub>6</sub> solutions in 5 mm tubes which were flame-sealed under vacuum and were referenced to TMS using the residual protons or the carbons of deuterated benzene at δ 7.15 ppm or δ 128 ppm, respectively. Melting points (uncorrected) were obtained with a Thomas-Hoover Unimelt apparatus and capillaries were flame-sealed under argon. Crystals

used in the x-ray analyses were flame-sealed in 0.7 mm thin-walled glass capillaries. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, New York.

### Syntheses

[*t*-Bu<sub>2</sub>GaAs(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (I) by salt elimination *t*-Bu<sub>2</sub>GaCl (0.14 g, 0.75 mmol) in C<sub>6</sub>H<sub>6</sub> (20 mL) and LiAs(SiMe<sub>3</sub>)<sub>2</sub>•2THF (0.26 g, 0.75 mmol) in C<sub>6</sub>H<sub>6</sub> (10 mL) were combined in a 100-mL one-necked round-bottomed flask equipped with a Teflon® valve and a magnetic stirbar. After one freeze-pump-thaw cycle of the solution, followed by stirring at room temperature for 48 h, the volatiles were removed *in vacuo* and pentane (20 mL) was added to the remaining solid. Filtration, followed by removal of the pentane from the filtrate, afforded a white solid which was subsequently recrystallized from pentane at -15 °C as colorless crystals of I, some of which were suitable for single-crystal X-ray analysis (0.27 g, 72% yield), mp 90-95 °C. Anal. Calcd (Found) for C<sub>28</sub>H<sub>72</sub>As<sub>2</sub>Ga<sub>2</sub>Si<sub>4</sub>: C, 41.50 (41.66); H, 8.95 (8.96). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.45 (s, 18 H, SiMe<sub>3</sub>), 1.25 (s, 18 H, CMe<sub>3</sub>).

*t*-Bu<sub>2</sub>GaAs(SiMe<sub>3</sub>)<sub>2</sub>Ga(*t*-Bu)<sub>2</sub>Cl (II) by reaction of *t*-Bu<sub>2</sub>GaCl with I (2:1 mole ratio). Fifteen minutes after combining *t*-Bu<sub>2</sub>GaCl (7.0 mg, 0.032 mmol) and I (13 mg, 16 mmol) in C<sub>6</sub>D<sub>6</sub> (1 mL) in an NMR tube, the <sup>1</sup>H NMR spectrum of the resulting clear solution contained two resonances [δ 0.46 (s, 18 H, SiMe<sub>3</sub>), 1.34 (s, 18 H, CMe<sub>3</sub>)] indicative of II [subsequently obtained <sup>13</sup>C{<sup>1</sup>H} NMR: δ 6.81 (s, SiMe<sub>3</sub>), 30.95 (s, CMe<sub>3</sub>)]. After opening the NMR tube in the Dri-Lab and transferring its contents to a glass vial, evaporation of the solvent afforded a white solid which was

dissolved in pentane. On cooling to  $-15\text{ }^{\circ}\text{C}$ , colorless crystals of **II**, some of which were suitable for single-crystal X-ray analysis, were obtained in nearly quantitative yield, mp  $85\text{--}100\text{ }^{\circ}\text{C}$  (dec). Anal. Calcd (Found) for  $\text{C}_{22}\text{H}_{54}\text{AsClGa}_2\text{Si}_2$ : C, 42.30 (41.94); H, 8.71 (8.82).

### Attempted Syntheses

$[\text{t-Bu}_2\text{GaAs}(\text{SiMe}_3)_2]_2$  (**I**) by dehalosilylation (reactants in a 1:1 mole ratio).  $\text{t-Bu}_2\text{GaCl}$  (0.22 g, 1.0 mmol) in  $\text{C}_6\text{H}_6$  (35 mL) and  $(\text{Me}_3\text{Si})_3\text{As}$  (0.30 g, 1.0 mmol) in  $\text{C}_6\text{H}_6$  (5 mL) were combined in a 100-mL one-necked round-bottomed flask equipped with a Teflon<sup>®</sup> valve and a magnetic stirbar. After one freeze-pump-thaw cycle of the solution, followed by stirring at room temperature for 6 days, the solvent was removed *in vacuo* leaving solid material, which on subsequent recrystallization from a pentane-ligroin mixture afforded large colorless crystals of  $\text{t-Bu}_2\text{GaCl}$  [mp  $170\text{--}172\text{ }^{\circ}\text{C}$  and  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.26 (s) are comparable to lit values]. Most of this starting material was recovered on subsequent concentration and cooling of the pentane-ligroin solution. Repeating the reaction using the same stoichiometry, but with heating at  $80\text{ }^{\circ}\text{C}$  for 5 d, afforded only starting materials.

$\text{t-Bu}_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{t-Bu})_2\text{Cl}$  (**II**) by dehalosilylation (reactants in a 2:1 mole ratio). In a manner similar to that described above, reaction of  $(\text{Me}_3\text{Si})_3\text{As}$  with 2 eq of  $\text{t-Bu}_2\text{GaCl}$  at room temperature and at  $80\text{ }^{\circ}\text{C}$  for 6 days did not afford **II**, and the latter starting material was recovered nearly quantitatively.



### *X-Ray Crystal Structure Analysis of I and II*

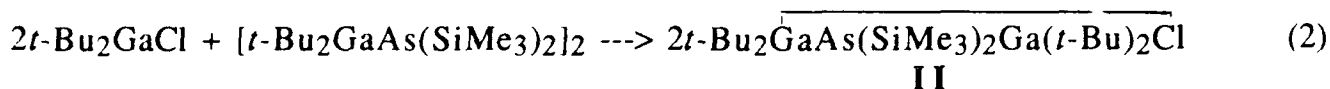
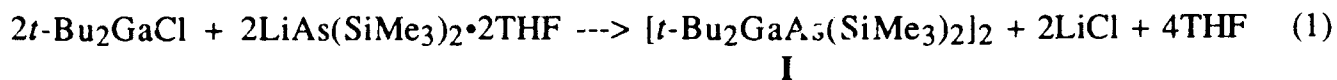
All measurements were performed on an Enraf-Nonius CAD-4 diffractometer (Cu-K $\alpha$  radiation,  $\lambda = 1.5418$  Å; incident-beam graphite monochromator). Intensity data were corrected for the usual Lorentz and polarization effects; empirical absorption corrections, based on the  $\Phi$ -dependency of the intensities of several reflections measured at  $\psi$  ca. 90°, were also applied. Both crystal structures were solved by the heavy-atom approach. For compound I, the systematic absences,  $hkl$  when  $h+k \neq 2n$ , are consistent with space groups  $C2$ ,  $Cm$ , and  $C2/m$ . Coordinates for the Ga and As atoms, derived from the Patterson map, were compatible with space group  $C2/m$ , and so all further calculations were performed using the equivalent positions of this space group. A weighted  $F_o$  Fourier synthesis phased by these two atoms yielded positions for the Si and C atoms and, moreover, identified the Ga and As atoms. For compound II, the systematic absences,  $hkl$  when  $h+k \neq 2n$  and  $h0l$  when  $l \neq 2n$ , are accommodated by the space groups  $Cc$  and  $C2/c$ . Interpretation of the vector peaks in the Patterson map yielded coordinates for the Ga and As atoms and established that the correct choice was the centrosymmetric space group  $C2/c$  with the As and Cl atoms lying on a crystallographic  $C_2$  symmetry axis. Coordinates for the other non-hydrogen atoms were derived from a weighted  $F_o$  Fourier synthesis phased by the Ga and As atoms. Non-hydrogen atom positional and thermal parameters (at first isotropic, then anisotropic) for both compounds were adjusted by means of several rounds of full-matrix least-squares calculations. In the later cycles, hydrogen atoms were included at their calculated positions (C-H = 1.05 Å) and an extinction correction was refined. A final difference Fourier

synthesis contained no unusual features. Crystallographic calculations were performed on PDP11/44 and MicroVAX computers by use of the Enraf-Nonius Structure Determination Package (SDP). For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from *International Tables for X-Ray Crystallography*, Vol. IV, The Kynoch Press, Birmingham, U.K. In the least-squares iterations,  $\Sigma w\Delta^2$  [ $w = 1/\sigma^2(|F_o|)$ ,  $\Delta = (|F_o| - |F_c|)$ ] was minimized. Further details of data collection and refinement are in Table I. Selected bond lengths, bond angles and torsion angles are in Tables II and III. Supplementary material: atomic coordinates, thermal parameters, bond lengths and angles, and crystal data have been deposited at the Cambridge Crystallographic Data Centre.

## RESULTS AND DISCUSSION

No reactions occurred at room temperature or at 80 °C in either the 1:1 or the 2:1 mole ratio mixture of *t*-Bu<sub>2</sub>GaCl and (Me<sub>3</sub>Si)<sub>3</sub>As in benzene. This is in contrast to results obtained by us when one or two equivalents of other dialkylgallium chlorides were allowed to react with one equivalent of the same silylarsine. For example, for the equimolar reaction using (Me<sub>3</sub>SiCH<sub>2</sub>)<sub>2</sub>GaCl, mixed-bridge **III** and other uncharacterized products were produced;<sup>4</sup> whereas, in the case of (Me<sub>3</sub>CCH<sub>2</sub>)<sub>2</sub>GaCl the adduct (Me<sub>3</sub>CCH<sub>2</sub>)<sub>2</sub>Ga(Cl)•As(SiMe<sub>3</sub>)<sub>3</sub> was isolated.<sup>5</sup> Furthermore, the 2:1 mole ratio reactions afforded the mixed-bridge species **III** and **IV**, respectively.

Nevertheless, by taking advantage of the metathetical salt elimination-bridge redistribution route, the desired *tert*-butyl containing compounds were accessible. Thus, as illustrated by equations 1 and 2, the reaction of



$t\text{-Bu}_2\text{GaCl}$  with  $\text{LiAs}(\text{SiMe}_3)_2 \cdot 2\text{THF}$  in benzene at room temperature yields dimer **I** in 72% yield, and redistribution of the latter with  $t\text{-Bu}_2\text{GaCl}$  affords mixed-bridge **II**, quantitatively. Obviously, the bulk of the *tert*-butyl group is such that interaction between  $t\text{-Bu}_2\text{GaCl}$  and  $(\text{Me}_3\text{Si})_3\text{As}$  can not be realized and thus result in dehalosilylation. On the other hand, the bulk of this particular alkyl group is not so great that it prohibits dimer and mixed-bridge formation, when the appropriate pathways to these species are found.

Crystals of **I** and **II** suitable for X-ray diffraction studies were grown from pentane. Crystallographic data are provided in Table 1. ORTEP diagrams showing the atom numbering schemes and the solid-state conformations of **I** and **II** are presented in Figure 1 and 2, respectively. Tables 2 and 3 list selected bond lengths and angles for **I** and **II**, respectively.

Dimer **I** crystallizes in the monoclinic system, space group  $C2/m$ , with only two formula units per unit cell. The As atoms lie on a crystallographic  $C_2$  axis and a mirror plane of symmetry bisects the Ga atoms, the central carbons of the *t*-Bu groups and one of their Me groups. The molecule has overall  $C_{2h}$  symmetry and thus the  $(\text{GaAs})_2$  ring is constrained to be perfectly flat. Comparison of the bond distances and angles of **I** with those of **V** and **VI** is very informative and reflects the greater amount of

steric crowding present in **I** where bond length extension is evident in all bonds involving the ring atoms. Thus, the Ga-As bond length of 2.630(1) Å in **I** is significantly longer than the means in **V** (2.567 Å) and **VI** (2.587 Å), the As-Si bond length in **I** [2.400(2) Å] is longer than the approximately equal mean values of 2.357 Å in **V** and 2.363 Å in **VI**, and the mean Ga-C bond length at 2.031 Å in **I** is also greater than the corresponding values of 1.990 Å in **V** and 1.997 Å in **VI**. In common with **V** and **VI**, the Ga-As-Ga angle [94.85(3)°] is greater than the As-Ga-As angle [85.14(3)°]; in **V** the Ga-As-Ga angle is 93.91(2)° and the mean As-Ga-As angle is 86.09°, while in **VI** the mean Ga-As-Ga angle is 94.97° and the As-Ga-As angle is 85.02(3)°. The exocyclic C-Ga-C and Si-As-Si bond angles at 114.3(3)° and 95.67(6)° in **I** are both considerably smaller than the corresponding angles in **V** [mean 123.9° and 103.66(6)°] and **VI** [135.2(3)° and 102.32(7)°].

Compound **II** crystallizes in the monoclinic system, space group  $C2/c$  with only four formula units per unit cell. The molecule lies on a crystallographic  $C_2$  symmetry axis which passes through the As and Cl atoms, and, accordingly, the  $\overline{\text{Ga-As-Ga-Cl}}$  is planar. As with dimer **I**, comparison of distances and angles in **II** with corresponding values in **III** and **IV** provides an indication of the effects of the increased steric crowding associated with the presence of the bulky *t*-Bu substituents. The As-Ga distance of 2.577(1) Å in **II** is considerably greater than the means of 2.504 Å in **III** and 2.521 Å in **IV**, the As-Si length of 2.393(2) Å is longer than the means of 2.348 Å and 2.358 Å in **III** and **IV**, respectively, and the mean Ga-C distance of 2.017 Å is slightly longer than the mean of 1.990 Å in **III** and much longer than the mean of 1.966 Å in **IV**. In contrast to these differences, the Ga-Cl bond length of 2.426(1) Å in planar

**II** is similar to the means of 2.432 Å in puckered **III** and 2.425 Å in planar **IV**, and thus it remains fairly constant. Closure of the exocyclic bond angles subtended at Ga and As reflects steric compression at these centers. The Si-As-Si angle in **II** at 97.32(5)° is considerably smaller than the corresponding angles in **III** [108.64(6)°] and **IV** [105.39(5)°], and the C-Ga-C angle of 120.8(3)° in **II** is also less than the means of 123.6° and 127.7° in **III** and **IV**, respectively.

More severe bond strain in group 13-group 15 dimers vs. their chloro-bridged analogs is manifested in the consistently greater values of the Ga-As distances in dimeric **I**, **V**, and **VI** where they exceed those in **II**, **III**, and **IV** by 0.053 Å, 0.063 Å, and 0.066 Å, respectively. In addition, the increased steric compression present in the dimers is reflected in the fact that their Si-As-Si angles are smaller:  $\Delta = 1.7^\circ$  in **I** vs. **II**,  $\Delta = 5.0^\circ$  in **V** vs. **III**, and  $\Delta = 3.0^\circ$  in **VI** vs. **IV**. These appear to be general features of this class of compounds as like differences between corresponding lengths ( $\Delta$  0.051 Å, 0.052 Å) and angles ( $\Delta$  3.3°, 5.4) have recently been found in pairs of In-As and In-P analogues [(Me<sub>3</sub>SiCH<sub>2</sub>)<sub>2</sub>InM(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> and (Me<sub>3</sub>SiCH<sub>2</sub>)<sub>2</sub>InM(SiMe<sub>3</sub>)<sub>2</sub>In(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>Cl, M = As,<sup>6</sup> P.<sup>7</sup>

**Acknowledgment.** The financial support for this work by the Office of Naval Research is gratefully acknowledged.

**Supplementary Material Available:** Tables of atomic coordinates, thermal parameters, and complete lists of interatomic distances and angles for **I** and **II**, (9 pages); a listing of observed and calculated structure amplitudes for **I** and **II** (31 pages).

## References

- (1) A. H. Cowley and R. A. Jones, *Angew. Chem. Int. Ed. Engl.* 1989, **28**, 1208.
- (2) C. G. Pitt, A. P. Purdy, K. T. Higa and R. L. Wells, *Organometallics* 1986, **5**, 1266.
- (3) C. G. Pitt, K. T. Higa, A. T. McPhail and R. L. Wells, *Inorg. Chem.* 1986, **25**, 2483.
- (4) R. L. Wells, J. W. Pasterczyk, A. T. McPhail, J. D. Johansen and A. Alvanipour, *J. Organomet. Chem.* 1991, **407**, 17.
- (5) R. L. Wells, A. T. McPhail, J. W. Pasterczyk and A. Alvanipour, *Organometallics* 1991, *submitted*.
- (6) R. L. Wells, L. J. Jones, A. T. McPhail and A. Alvanipour, *Organometallics* 1991, **10**, 2345
- (7) R. L. Wells, A. T. McPhail and M. F. Self, *Organometallics* 1991, *in press*.
- (8) A. H. Cowley, B. L. Benac, J. G. Ekerdt, R. A. Jones, K. B. Kidd, J.Y. Lee and J. E. Miller *J. Am. Chem. Soc.* 1988, **110**, 6248.
- (9) K. T. Higa and C. George *Organometallics* 1990, **9**, 275.
- (10) G. Becker, G. Gutekunst and H. J. Wessely, *Z. Anorg. Allg. Chem.* 1980, **462**, 113.

Captions to Figures

Figure 1. ORTEP diagram (30% probability ellipsoids) showing the solid-state structure of  $[t\text{-Bu}_2\text{GaAs}(\text{SiMe}_3)_2]_2$  (I); hydrogen atoms have been omitted for clarity.

Figure 2. ORTEP diagram (40% probability ellipsoids) showing the solid-state structure of  $t\text{-Bu}_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(t\text{-Bu})_2\text{Cl}$  (II); hydrogen atoms have been omitted for clarity.

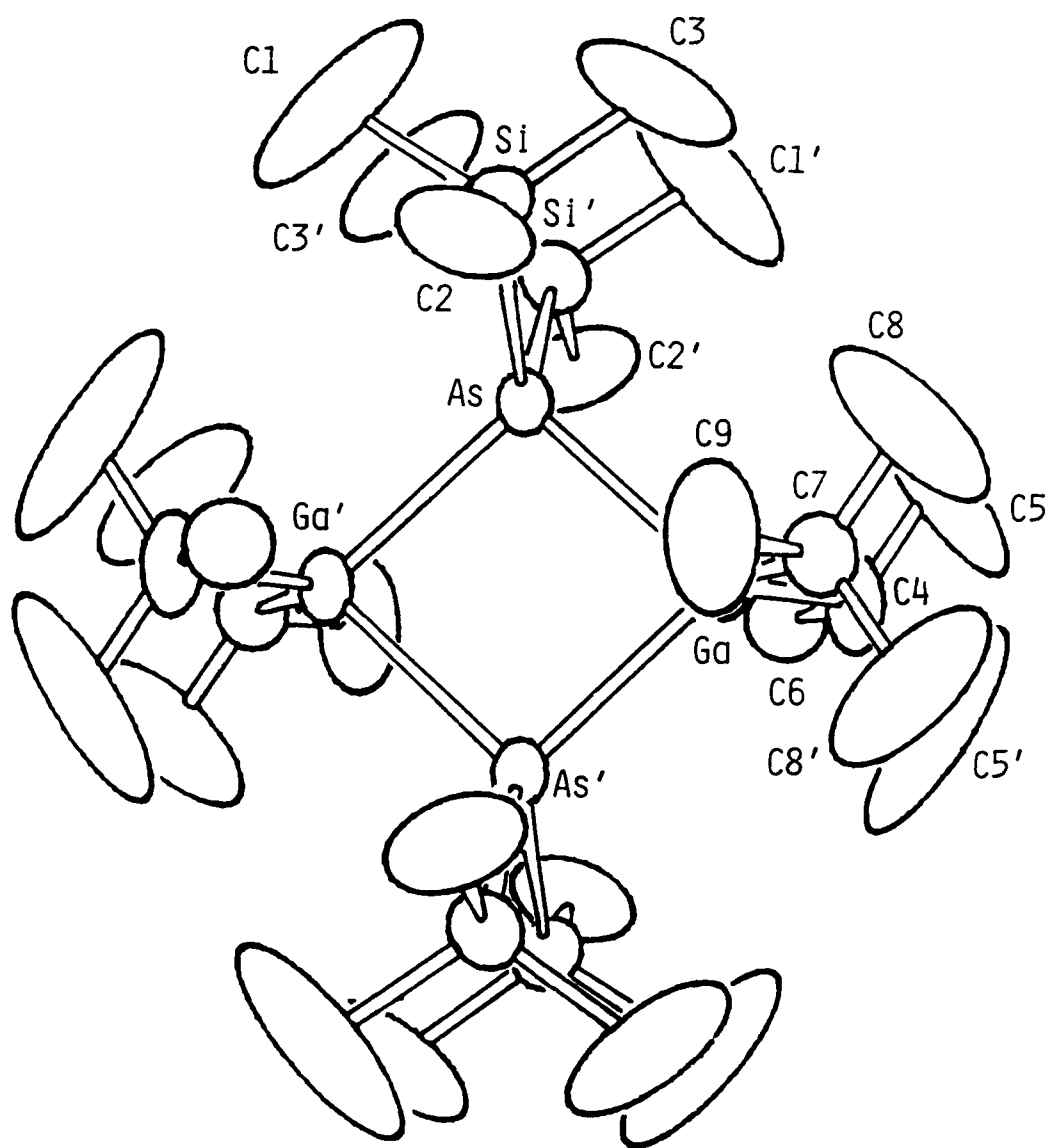


Figure 1



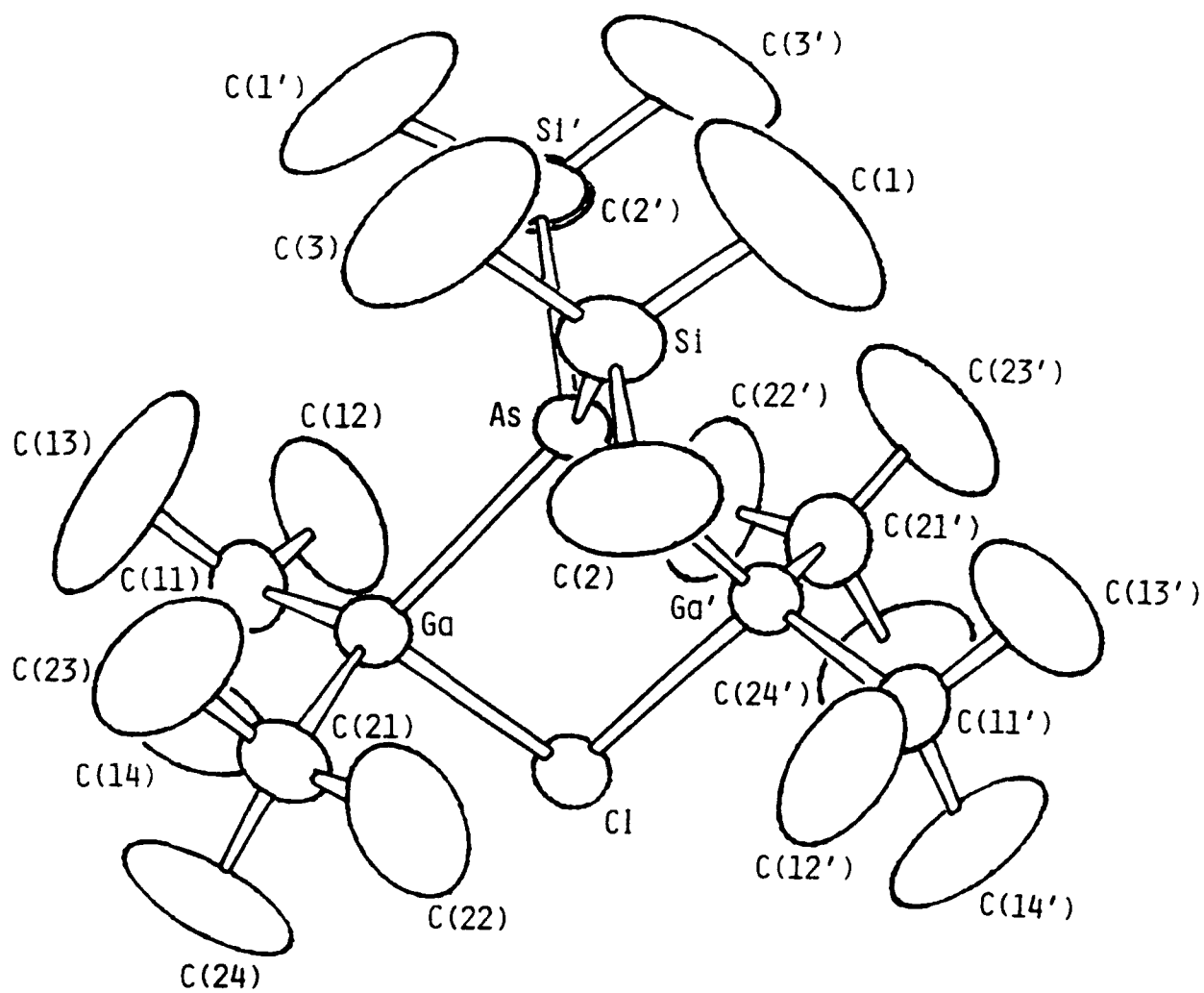


Figure 2

**Table 1. Crystallographic Data and Measurements<sup>a</sup> for**  
**[*t*-Bu<sub>2</sub>GaAs(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (I) and *t*-Bu<sub>2</sub>GaAs(SiMe<sub>3</sub>)<sub>2</sub>Ga(*t*-Bu)<sub>2</sub>Cl (II)**

|   | I   | II  |
|---|---|---|
| Formula   | C <sub>28</sub> H <sub>72</sub> As <sub>2</sub> Ga <sub>2</sub> Si <sub>4</sub> | C <sub>22</sub> H <sub>54</sub> AsClGa <sub>2</sub> Si <sub>2</sub> |
| Formula weight                                    | 810.51  | 624.66  |
| Crystal system                                    | monoclinic  | monoclinic  |
| Space group                                       | <i>C</i> 2/ <i>m</i> ( <i>C</i> <sup>3</sup> <sub>2h</sub> )                    | <i>C</i> 2/ <i>c</i> ( <i>C</i> <sup>6</sup> <sub>2h</sub> )        |
| <i>a</i> (Å)                                      | 18.188(2)   | 20.872(4)   |
| <i>b</i> (Å)                                      | 13.017(1)   | 9.798(1)  |
| <i>c</i> (Å)                                      | 9.916(1)  | 19.397(4)   |
| β (°)   | 118.54(1)   | 124.13(2)   |
| No. of orient. refls; θ (°) range                 | 25; 42-48   | 25; 42-47   |
| <i>V</i> (Å <sup>3</sup> )                        | 20624(8)  | 3284(2)   |
| <i>Z</i>  | 2   | 4   |
| <i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )   | 1.305   | 1.264   |
| μ(Cu- <i>K</i> α rad., λ = 1.5418 Å)              | 46.4  | 46.5  |
| Temp. (°C)  | 25  | 25  |
| Crystal dimensions (mm)                           | 0.18x0.24x0.28  | 0.50x0.50x0.50  |
| <i>T</i> <sub>max</sub> : <i>T</i> <sub>min</sub> | 1.00:0.72   | 1.00:0.90   |
| Scan type   | ω-2θ  | ω-2θ  |
| Scan width (°)                                    | 1.15 + 0.14tanθ   | 1.00 + 0.14tanθ   |
| θ <sub>max</sub> . (°)                            | 75  | 75  |
| Intensity control refls.                          | 331, 22 $\bar{3}$ , 2 $\bar{2}$ 3, 3 $\bar{3}$ 1                                | 53 $\bar{2}$ , 242, 5 $\bar{3}$ 2, 2 $\bar{4}$ 2                    |

Table 1 (continued)

|  |                         |                         |
|--|-------------------------|-------------------------|
| Variation; repeat time (h)                         | <2%; 2                  | <1%; 2                  |
| No. of rfls. (+h,+k,±l) recded                     | 2279                    | 3489                    |
| No. of non-equiv. rfls. recded                     | 2210                    | 3380                    |
| $R_{\text{merge}}$ (on $I$ )                       | 0.016                   | 0.020                   |
| No. of rfls. retained [ $I > 3.0\sigma(I)$ ]       | 1798                    | 2812                    |
| No. of parameters refined                          | 91                      | 129                     |
| Extinction correction                              | $7.7(2) \times 10^{-6}$ | $1.8(1) \times 10^{-6}$ |
| $R$ ( $R_w$ ) <sup>a</sup>                         | 0.057(0.079)            | 0.055 (0.081)           |
| Goodness-of-fit <sup>b</sup>                       | 2.77                    | 2.70                    |
| Max. shift:esd in final<br>least-sq. cycle         | 0.03                    | 0.02                    |
| Final $\Delta\rho(\text{e}/\text{\AA}^3)$ max; min | 0.90; -0.86             | 0.32; -0.41             |

---

<sup>a</sup> $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ ;  $R_w = [\Sigma w (|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$ ;  $\Sigma w \Delta^2 [w = 1/\sigma^2(|F_o|), \Delta = (|F_o| - |F_c|)]$  was minimized.

<sup>b</sup>Goodness-of-fit =  $[\Sigma w \Delta^2 / (N_{\text{observations}} - N_{\text{parameters}})]^{1/2}$ .

**Table 2. Selected Bond Lengths (Å) and Angles (deg) for  
[*t*-Bu<sub>2</sub>GaAs(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (I), with Estimated Standard  
Deviations in Parentheses.**

---

(a) Bond lengths

|       |          |         |          |
|-------|----------|---------|----------|
| As-Ga | 2.630(1) | Ga-C(4) | 2.025(9) |
| As-Si | 2.400(2) | Ga-C(7) | 2.036(6) |

(b) Bond angles

|              |           |              |          |
|--------------|-----------|--------------|----------|
| Ga-As-Si     | 116.65(3) | As-Si-C(1)   | 110.8(4) |
| Ga-As-Si'    | 117.36(5) | As-Si-C(2)   | 117.3(3) |
| Ga-As-Ga'    | 94.85(3)  | As-Si-C(3)   | 110.3(4) |
| Si-As-Si'    | 95.67(6)  | C(1)-Si-C(2) | 102.8(6) |
| As-Ga-As'    | 85.15(3)  | C(1)-Si-C(3) | 110.6(6) |
| As-Ga-C(4)   | 113.2(1)  | C(2)-Si-C(3) | 104.6(4) |
| As-Ga-C(7)   | 113.9(2)  |              |          |
| C(4)-Ga-C(7) | 114.3(3)  |              |          |

**Table 3. Selected Bond Lengths (Å) and Angles (deg) for  $t\text{-Bu}_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(t\text{-Bu})_2\text{Cl}$  (II), with Estimated Standard Deviations in Parentheses.**

(a) Bond lengths

|       |          |          |          |          |          |
|-------|----------|----------|----------|----------|----------|
| As-Ga | 2.577(1) | Ga-Cl    | 2.426(1) | Ga-C(21) | 2.025(4) |
| As-Si | 2.393(2) | Ga-C(11) | 2.009(4) |          |          |

(b) Bond angles

|             |           |                |          |
|-------------|-----------|----------------|----------|
| Ga-As-Si    | 118.12(2) | C(11)-Ga-C(21) | 120.8(3) |
| Ga-As-Ga'   | 89.49(2)  | Ga-Cl-Ga'      | 96.81(7) |
| Ga-As-Si'   | 117.84(2) | As-Si-C(1)     | 108.5(3) |
| Si-As-Si'   | 97.32(5)  | As-Si-C(2)     | 117.4(3) |
| As-Ga-Cl    | 86.85(4)  | As-Si-C(3)     | 110.0(3) |
| As-Ga-C(11) | 115.4(2)  | C(1)-Si-C(2)   | 107.3(6) |
| As-Ga-C(21) | 116.9(2)  | C(1)-Si-C(3)   | 109.2(5) |
| Cl-Ga-C(11) | 103.7(2)  | C(2)-Si-C(3)   | 104.2(4) |
| Cl-Ga-C(21) | 105.0(2)  |                |          |

(c) Torsion angles<sup>a</sup>

|                 |            |                 |           |
|-----------------|------------|-----------------|-----------|
| Si-As-Ga-Cl     | -121.65(5) | Si'-As-Ga-Cl    | 121.89(5) |
| Si-As-Ga-C(11)  | 134.7(2)   | Si'-As-Ga-C(11) | 18.3(2)   |
| Si-As-Ga-C(21)  | -16.4(2)   | Si'-As-Ga-C(21) | -132.9(2) |
| Ga'-As-Ga-Cl    | 0.0(-)     | As-Ga-Cl-Ga'    | 0.0(-)    |
| Ga'-As-Ga-C(11) | -103.6(2)  | C(11)-Ga-Cl-Ga' | 115.4(2)  |
| Ga'-As-Ga-C(21) | 105.2(2)   | C(21)-Ga-Cl-Ga' | -117.0(2) |

<sup>a</sup>The torsion angle A-B-C-D is defined as positive if, when viewed along the B-C bond, atom A must be rotated clockwise to eclipse atom D.

TECHNICAL REPORT DISTRIBUTION LIST - GENERAL

Office of Naval Research (2)  
Chemistry Division, Code 1113  
800 North Quincy Street  
Arlington, VA 22217-5000

Commanding Officer (1)  
Naval Weapons Support Center  
Dr. Bernard E. Douda  
Crane, IN 47522-5050

Dr. James S. Murday (1)  
Chemistry Division, Code 6100  
Naval Research Laboratory  
Washington, DC 20375-5000

Dr. Richard W. Drisko (1)  
Naval Civil Engineering Lab.  
Code L52  
Port Hueneme, CA 93043

Dr. Robert Green, Director (1)  
Chemistry Division, Code 385  
Naval Weapons Center  
China Lake, CA 93555-6001

Dr. Harold H. Singerman (1)  
David Taylor Research Center  
Code 283  
Annapolis, MD 21402-5067

Dr. Eugene C. Fischer (1)  
Code 2840  
David Taylor Research Center  
Annapolis, MD 21402-5067

Chief of Naval Research (1)  
Special Assistant for Marine  
Corps Matters  
Code 00MC  
800 North Quincy Street  
Arlington, VA 22217-5000

Dr. Elek Lindner (1)  
Naval Ocean Systems Center  
Code 52  
San Diego, CA 92152-5000

Defense Technical  
Information Center (2)  
Building 5, Cameron Station  
Alexandria, VA 22314